



Impact of amino acids, organic solvents and surfactants on azo-hydrazone tautomerism in Methyl Red: spectral-luminescent and nonlinear optical properties

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Abstract

Azo-linkage in compounds offer broad-spectrum photochromic and nonlinear optical (NLO) properties owing to their architectural flexibility. The present work reports the effects of amino acids, organic solvents and ionic surfactants on the azo-hydrazone tautomerism and hence NLO properties of Methyl Red (MR) dye via the Z-scan technique and spectral-luminescent measurements. From the spectral measurements, the azo-hydrazone transition in MR was observed with the addition of amino acids (L-Phenylalanine and L-Alanine) and ionic surfactants (AOT and CTAB) probably due to the charge interaction. While, this azo-hydrazone switching was not observed with the change of solvent polarity. Moreover, with the provision of the quantum perturbation theory, it was observed that the NLO values of MR also transmuted by changing the concentration of amino acids and surfactants as well as solvent polarity probably due to the fluctuation of the dipole moment of dye during tautomerism and thermal conductivity of solvent, respectively. The results can be integrated into the possible future applications of azo-based molecules in novel photonic and optoelectronic devices.

Keywords Photochromic · Optics · Tautomerism · Amino acid · Surfactant

1 Introduction

The emergence of smart photonics and optoelectronics has caused worldwide concern about the optical nonlinearities of organic molecules. Among numerous organic molecular systems, the azo linkage in compounds has significant nonlinear optical (NLO) sensitivity due to their architectural flexibility (Afzal et al. 2016; Matazo et al. 2008;

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He and Wang 2008; Lee et al. 2005; Sindhu Sukumaran and Ramanlingam 2006). The electronic nonlinearity can be induced by population redistribution of electronic clouds that leads the perturbation of dipole moment in azo-containing molecules. The *cis*–*trans* photoisomerization of azo molecules provides a convenient approach to modify their optical nonlinearity, photoswitchability and other molecular properties, depending on the chemical environment (Li et al. 2017; Liaros et al. 2013; Sousani et al. 2016; Virkki et al. 2016; Schulze et al. 2015; Bronner et al. 2013).

In the present study, we examined the effects of amino acids, organic solvents and ionic surfactants on the azo-hydrazone tautomerism and hence NLO properties of Methyl Red (MR) dye via the Z-scan technique and spectral-luminescent measurements. Methyl-Red (2-(*N,N*-dimethyl-4-aminophenyl) azobenzene carboxylic acid) is an azo-linked ($-N=N-$) organic dye that exhibits photoinduced azo-hydrazone (or ammonium-azonium) tautomerism (basic molecular structure of MR with the corresponding tautomeric equilibria (azo-hydrazone) is shown in Fig. 1) and therefore reflects large optical nonlinearities (Christodoulides et al. 2010).

Methyl red is a commonly used acid–base indicator and changes color at a pH of 5.5 (Mendham et al. 2004; Lee et al. 2011). It is widely used for carbohydrate and lactic acid detections as well as for salivary analysis in glucose biosensors (Vallee and Gibson 1948). It has been used as pH indicator in a glucose biosensor, which is used for salivary analysis (Soni and Jha 2015). The literature shows that the absorption maximum of the *trans*-conformer of MR is at 420 nm and that of the *cis*-conformer appears at 350 nm (Mukherjee and Bera 1998; Larsen and Perkins 2016). MR also show significant NLO properties and hence is a strong candidate for photonic applications (Li et al. 2017). But, most of the NLO properties of MR are investigated by continuous-wave (CW) laser (Zheng et al. 2015).

The present study describes the spectral and Z-scan techniques to measure the extent of NLO properties of MR in presence of various organic solvents (i.e. ethanol, DMSO and DMF), amino acids (i.e. L-Alanine and L-Phenylalanine) and ionic surfactants (i.e. AOT and CTAB). As most of the aqueous solution of amino acids shows optical transparency, so the effect of L-Alanine and L-Phenylalanine on the NLO properties of MR were studied with the addition of Neutral Red (as a photosensitizer molecule).

A NLO of the liquid media with different molecular length scale was studied before. It was demonstrated that the length scale of sample can change the NLO properties

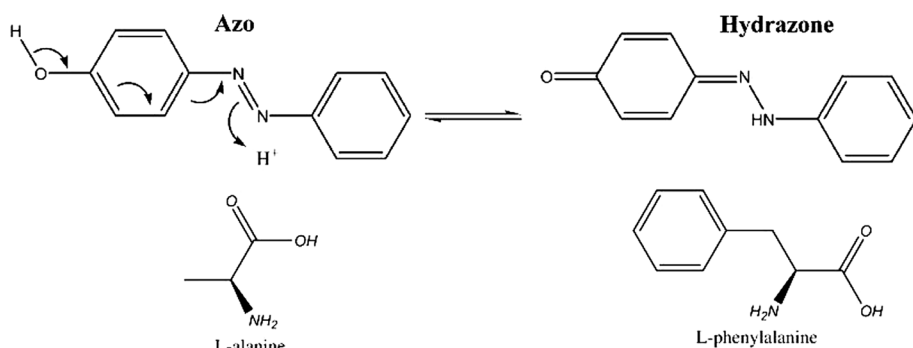


Fig. 1 The molecular structure of Methyl Red (MR) with the corresponding tautomeric azo-hydrazone equilibrium

(Sahraoui and Rivoire 1997). Since, the amino acids have different length scale, thus they have different effect on NLO properties of dye.

Moreover, to support the NLO measurements of MR, obtained from photophysical techniques, the Z-scan is also utilized as an effective tool to measure its nonlinear absorption (β), nonlinear refractive index (n_2), second-order hyperpolarizabilities (γ_R), and the real part of the third-order susceptibility (χ_R). The z-scan instrument have open and close aperture detector that the normalized open aperture curve can be explained by Eqs. (1) (Khadem Sadigh et al. 2017).

$$T_{OA} = \sum_{n=0} (-q_0)^n \times (n+1)^{-\frac{3}{2}} \quad (1)$$

where q_0 is

$$q_0 = \beta I_0 L_{eff} \left(1 + \left(\frac{z}{z_0} \right)^2 \right)^{-1} \quad (2)$$

In Eq. (2), L_{eff} is the effective thickness and z_0 is Rayleigh length, and β is the nonlinear absorption. The difference between peak and valley of the close aperture transmittances (ΔT_{p-v}) can be explained by (Saievar Iranizad et al. 2014; Gayathri and Ramalingam 2007):

$$\Delta T_{p-v} = 0.406(1-S)^{0.25} \Delta \Phi_0 \quad (3)$$

where $\Delta \Phi_0$ is the phase and S is the aperture parameter. The nonlinear refractive index (n_2) can be calculated from the ΔT_{p-v} by (Gayathri and Ramalingam 2007):

$$n_2 = (\lambda \Delta T_{p-v}) \cdot (2\pi L_{eff} I_0 (0.406)(1-S)^{0.25})^{-1} \quad (4)$$

2 Experimental

2.1 Materials

Methyl red dye (purity > 95%), Neutral Red, Sodium bis(2-ethylhexyl) sulfosuccinate (AOT) (purity > 99%), Cetyl trimethylammonium bromide (CTAB), L-Alanine and L-Phenylalanine amino acid (99% purity), dimethylformamide (DMF), dimethyl sulfoxide (DMSO), ethanol, L-Phenylalanine and L-Alanine were purchased from Sigma-Aldrich.

2.2 Preparation of solutions

Three types of solutions are prepared to study the linear and nonlinear optical properties of MR in different solution.

1. In the first part of the study, the photophysics of (a) MR in different solvent (Ethanol, DMSO, and DMF) at a dye concentration ($C_{dye} = 0.02$ mM), (b) MR in Ethanol–Water solutions (10% Ethanol) at a dye concentration ($C_{dye} = 0.083$ mM) at a constant AOT and

CTAB concentration ($C_{AOT}=2$ mM, $C_{CTAB}=2$ mM) are studied by spectrophotometer and fluorometer.

- In the second part of the study, the nonlinear optical properties of (a) MR in different solvent (Ethanol, DMSO, and DMF) at different dye concentration (C_{dye} between 0.01 and 0.05 mM), (b) MR mixed with DMSO-water solutions with different water percent at $C_{dye}=0.015$ mM for open aperture curves, and $C_{dye}=0.006$ mM for close aperture curves, (c) MR mixed with Ethanol–Water solutions (10% Ethanol) at $C_{dye}=0.024$ mM and different AOT concentration (0–4 mM) and Ethanol–Water solutions (10% Ethanol) at $C_{dye}=0.043$ mM and different CTAB concentration (0–6 mM) are studied by z-scan instrument.
- In the third part of the study, the nonlinear optical properties of MR mixed with Ethanol–Water solutions (10% Ethanol) at constant dye concentration ($C_{dye}=0.024$ mM for open aperture and $C_{dye}=0.008$ mM for close aperture) at different L-Phenylalanine and L-Alanine concentration. The effect of α -amino acid on the open aperture curves of Neutral Red are studied at different α -amino acid concentration and a constant dye concentration ($C_{dye}=0.1$ mM).

2.3 Characterization

The z-scan was recorded with cw laser ($\lambda=655$ nm—A TEM00 Gaussian and the power of focal point is 80mW), far away from the absorbance peak of the MR. While, the laser light (655 nm) do not linear absorption in MR. Thus, the damage cannot observed with thermal effect. The thickness of quartz cell is 1 mm and it is moving in the z-axis and the Rayleigh length is 1.55 mm. The UV-1650 PC spectrometer, and FP-6200 spectrofluorometer (Jasco) was used to study of absorbance and fluorescence spectra of samples.

3 Results and discussion

3.1 Photophysics of MR

The absorption and fluorescence spectra of MR in different solvents (Ethanol, DMSO, DMF) was recorded at $C_{dye}=0.02$ mM and the results are reported in Fig. 2a, b. The absorbance of MR in Ethanol shows two broad peaks around 403 and 498 nm that it is similar to the absorbance spectra of azo form of MR.

The lower the wavelength of the absorbance peak of MR in Ethanol change from 403 to 427 nm with the change of solvent from Ethanol ($\epsilon=2.25$) to DMSO ($\epsilon=46.7$). Thus, a red shift is observed by the change of solvents dielectric constant. Thus, the azo form of MR is sensitive to the polarity of solvents. The fluorescence spectra of MR in solvents show a main peak at 483 ± 1 nm and other three peaks.

The absorbance and fluorescence of MR in Ethanol–Water (10% Ethanol in Water) were also measured at constant dye and surfactant concentration ($C_{dye}=0.083$ mM, $C_{AOT}=2$ mM, $C_{CTAB}=2$ mM) and the results are shown in Fig. 2c, d. The absorbance spectra of MR in Ethanol–Water (10% Ethanol in Water) shows two broad peaks at $\lambda_{abs}=422$ nm and 519 nm. The red shift is observed with the change of solvent from Ethanol to Ethanol–Water (10% Ethanol in Water) that it is due to the increase of dielectric constant of solvent and the solubility reduction, Fig. 2c.

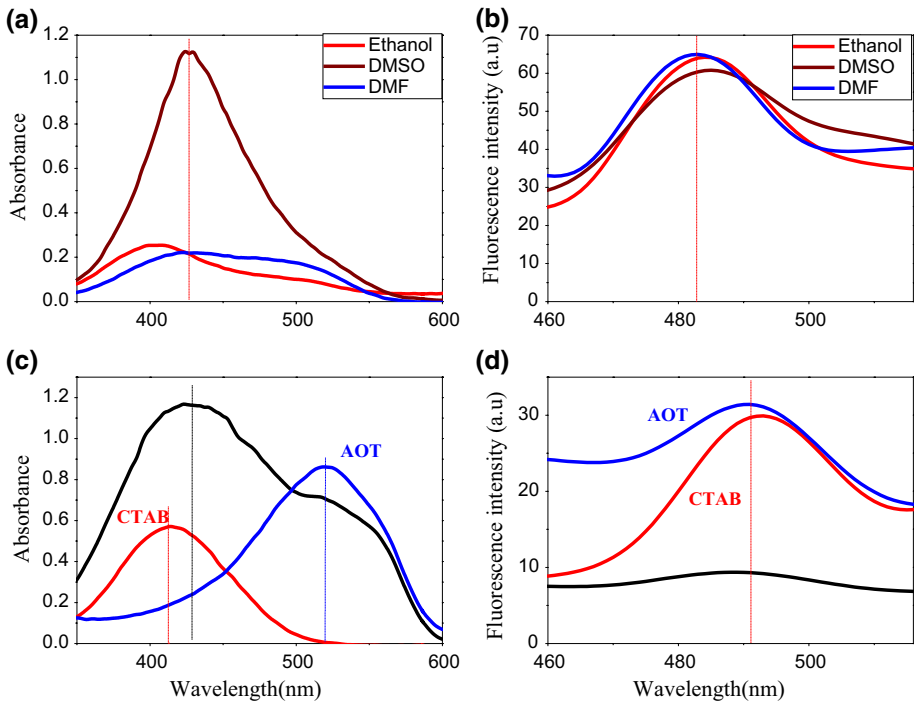


Fig. 2 **a, b** The absorption and fluorescence spectra of MR in different solvents (ethanol, DMSO, DMF) is studying at a constant dye concentration ($C_{dye}=0.02$ mM). **c, d** The absorption and fluorescence spectra of MR in Ethanol–Water (10% Ethanol) and Ethanol–Water–Surfactant (AOT, CTAB) at constant surfactant concentration ($C_{sur}=2$ mM) and a constant dye concentration ($C_{dye}=0.083$ mM)

The absorbance peak of MR in Ethanol–Water–AOT ($C_{dye}=83$ μ M, $C_{AOT}=2$ mM) shows a broad peak at $\lambda_{abs}=519$ nm that it is attributed to hydrazone form. The transfer from azo to hydrazone form is appeared by the increase of anionic AOT in Ethanol–Water solutions.

In the previous study, the interaction of MR with SDS (anionic surfactant) and CPS (cationic surfactant) is studied (Jirasová et al. 1990). In the mixture of MR with SDS and CPS binary system, the wavelength of absorbance peak doesn't change with the increase of surfactant (SDS and CPS) concentration, but a hypochromic effect is observed. It was observed that the dielectric constant value is reduced by the increase of CPS (a cationic surfactant) concentration in solutions and it's enhanced with SDS.

In Fig. 2c, a broad absorbance peak, at $\lambda_{abs}=414$ nm is observed in Ethanol–Water–CTAB solutions ($C_{dye}=83$ μ M, $C_{CTAB}=2$ mM) that it is due to the azo form of MR.

The fluorescence spectra of MR in Ethanol–Water (10% Ethanol in Water) show at 490 nm and other three peaks between 540 and 650 nm. With compare the fluorescence spectra of MR in Ethanol and Ethanol–Water solutions, the red shift is observed that it is due to the increase of dielectric constant of the solution by the increase of water percent, Fig. 2d. The fluorescence peak at 490 nm does not change by the increase of surfactant type. While the fluorescence intensity of MR is quenched by adding surfactants (AOT or CTAB) to solutions.

In this work, the theory is used to study the ground and excite dipole moment of MR in solutions. The theory can be described by the following equations (Gulseven and Sidir 2013; Sangsefedi et al. 2018; Peyghami et al. 2017; Shavakandi et al. 2017):

$$\nu_a - \nu_b = p_1 \times f(\varepsilon, n) + \text{const} \tag{5}$$

$$\nu_a + \nu_b = -p_2 \times (f(\varepsilon, n) + 2g(n)) + \text{const} \tag{6}$$

where, ν_a and ν_b are the wavenumbers of absorption and fluorescence of samples. The $f(\varepsilon, n)$ and $g(n)$ can be described by

$$f(\varepsilon, n) = \frac{2n^2 + 1}{n^2 + 1} \left[\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right] \tag{7}$$

and

$$g(n) = \frac{3}{2} \left[\frac{n^4 - 1}{(n^2 + 2)^2} \right] \tag{8}$$

In which ε and n are the permittivity and refractive index of the solvent, respectively. The ratio of the dipole moment of the excited state to the ground state can be described by the following equations (Shavakandi et al. 2017):

$$\frac{\mu_e}{\mu_g} = \frac{p_2 + p_1}{p_2 - p_1} \tag{9}$$

The ratio of the dipole moment (μ_e/μ_g) can be determined by Eq. (9) and the results are reported in Table 1.

The dipole moment ratio of MR in the solvent (Ethanol, DMSO, DMF, Ethanol–Water) is constant ($\mu_e/\mu_g = 1.57$). The dipole moment ratio of MR in Ethanol–Water–AOT ($\mu_e/\mu_g = 2.34$) is higher than Ethanol–Water–CTAB ($\mu_e/\mu_g = 1.63$) that it is due to the azo to hydrazone form transition. We can propose that the ground state dipole moment of dye (μ_g) in Ethanol–Water–AOT is higher than Ethanol–Water–CTAB.

Two reasons can change the value of μ_e/μ_g : firstly, the solubility of dye in solutions. It is known that the solubility of cationic dye decreases with reduction of anionic surfactant in solutions. The MR is a cationic dye that it can have an attractive interaction with anionic surfactant. In the previous study, the photophysics of Crocin in polar solvent and

Table 1 The ratio of the dipole moment of the excited state to the ground state (μ_e/μ_g) of MR in solvents (ethanol, DMSO, DMF) and solutions of Ethanol–Water (10% ethanol) and Ethanol–Water–surfactant (AOT, CTAB)

Solvent	C dye (mM)	C sur (mM)	Ethanol (%)	λ_{abs}	λ_{em}	$\nu_a + \nu_b$	$\nu_a - \nu_b$	$\frac{\mu_e}{\mu_g}$
Ethanol	0.02	–	–	403	483	45,492	4139	1.57 ± 0.07
DMSO	0.02	–	–	427	484	44,054	2783	1.57 ± 0.07
DMF	0.02	–	–	423	482	44,374	2906	1.57 ± 0.07
Ethanol–Water	0.083	–	10	422	488	44,131	3206	1.57 ± 0.07
Ethanol–Water–AOT	0.083	2	10	519	490	39,627	1121	2.34 ± 0.07
Ethanol–Water–CTAB	0.083	2	10	415	493	44,332	3813	1.63 ± 0.07

AOT–Water–Hexane is studied (Azarpour et al. 2018). Because of the interaction between Crocin with AOT surfactant, the solubility of Crocin in AOT–Water–Hexane is higher than other solvent. For this reason, the values of μ_c/μ_g of Crocin in AOT–Water–Hexane are greater than other polar solvent (Azarpour et al. 2018). Secondly, the change of the molecular structure of the dye can affect the value of μ_c/μ_g . In the case of the MR, the value of μ_c/μ_g change with of azo to hydrazone transition and it is not effect of solubility.

3.2 Nonlinear optical properties of MR: effect of surfactant and solvent

The NLO properties of azo dye (1-amino-2-hydroxy naphthalin sulfonic acid-[3-(4-azo)]-4-amino diphenyl sulfone) in ethanol have been studied with z-scan instrument with cw Laser and it is demonstrated that the azo dye are good candidates for optoelectronic application (YassinAl-Ahmad et al. 2012). Moreover, the NLO properties of *p*-aminoazobenzene (PAAB), *p*-dimethylamino benzene arsenic acid (PDBAA) and methyl orange (MO) were studied before. Between the azo dyes, PDBAA exhibited the biggest value of nonlinear refractive index (He and Wang 2008).

In this work, to study the solvent effect on nonlinear optical properties of MR, the mixture of different dye concentration in Ethanol, DMSO and DMF is studied by using Z-scan instrument. The normalized open aperture curves of MR in the different solvent are shown in Fig. 3a–c and the normalized close aperture of MR in Ethanol, DMSO and DMF are presented in Fig. 3d–f. The nonlinear absorption (β) of MR in solvents was extracted from the normalized open aperture curves and Eqs. (1) and (2). In general, in organic molecules, reverse saturation absorption has been explained using five level energy models and two photon absorption needs pulse laser with high intensity. Thus, in our case, RSA is occurred by cw laser in z-scan instrument.

The value of n_2 is extracted from the normalized close aperture curves and Eqs. (3) and (4). The values of β and n_2 are presented in Table 2. The third order susceptibility (real part) χ_R is found by using the equation (Han et al. 2018; Motiei et al. 2017):

$$\chi_R = 2n_2n_0^2\epsilon_0^2c \quad (10)$$

where n_0 is the refractive index and c is the light velocity, respectively. The hyperpolarizabilities, γ_R , can be calculated by Eq. (11) (Couris et al. 1995).

$$\gamma_R = \frac{\chi_R^{(3)}}{L^4N} \quad (11)$$

where L is the Lorenz parameters. The value of χ_R and γ_R of MR in solvents is calculated from Eqs. (10) and (11) and the results are summarized in Table 2. The value of β has increased from 4.24×10^{-7} to $6.00 \times 10^{-7} \text{ mw}^{-1}$ ($C_{\text{dye}}=0.02 \text{ mM}$) and the value of n_2 has increased from 7.00×10^{-12} to $11.27 \times 10^{-12} \text{ m}^2\text{W}^{-1}$ ($C_{\text{dye}}=0.004 \text{ mM}$) by the change of the solvent from Ethanol ($\epsilon=2.25$) to DMSO ($\epsilon=46.7$). MR is insoluble in water, and more soluble in organic solvents. Thus the MR solubility is reduced with an increase of polarity or dielectric constant of solvent. In general, the dye aggregation reduces with the increase of dye solubility and vice versa. From Fig. 2, the value of absorbance of MR in DMSO is higher than other solvent. Thus, the enhancement of nonlinear optical values can be due to increase of absorbance in solutions or the increase of dye aggregation.

To study the effect of solubility on the nonlinear optical properties, the mixture of dye with the DMSO–Water is studied at the different percent of water in DMSO. The

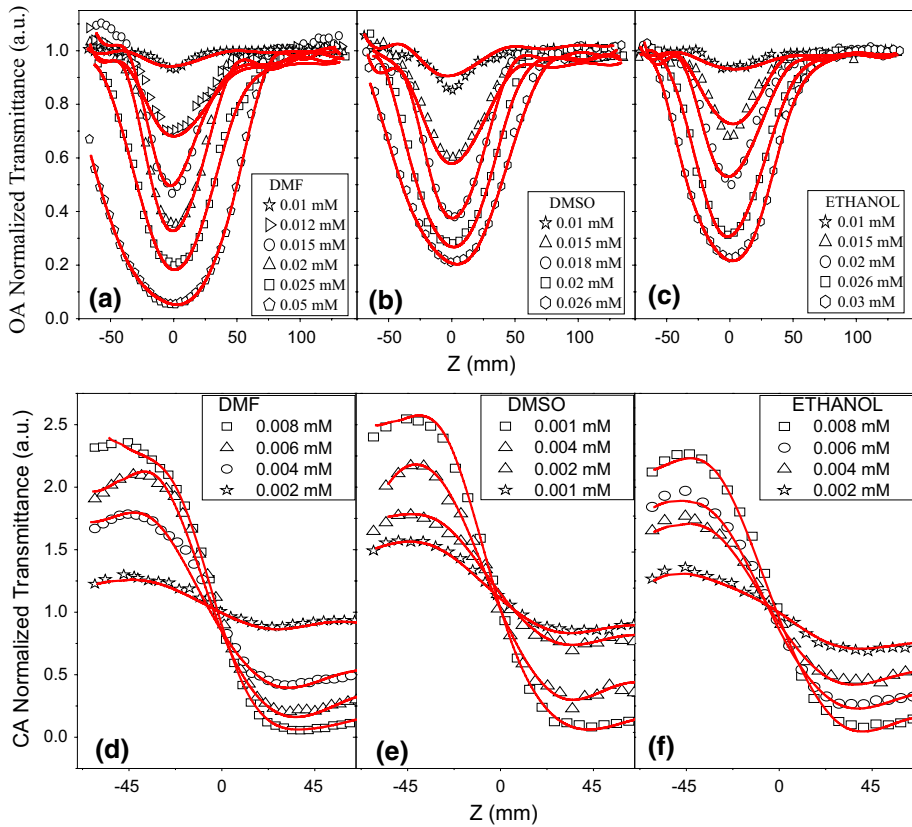


Fig. 3 a–c The open aperture curves of MR in different solvent and d–f The close aperture of MR in Ethanol, DMSO and DMF

open aperture and close aperture curves of MR in DMSO-Water solutions at different percent of water in DMSO (between 0 and 90%) at a constant dye concentration ($C_{\text{dye}} = 0.015$ mM for open aperture and $C_{\text{dye}} = 0.006$ mM for close aperture) are shown in Fig. 4. The values of β , n_2 , γ_R and χ_R are extracted and the results are summarized in Table 3. The values of β have increased from 2.68×10^{-7} to 6.46×10^{-7} mw^{-1} with an increase of water from 0 to 90% and the values of n_2 have increased from 5.88×10^{-12} to 16.51×10^{-12} m^2W^{-1} with the change of water from 0 to 60% in solutions. The same behavior is observed for γ_R and χ_R . By increase of water percent in DMSO, the dielectric constant of solutions is increased then the MR solubility is reduced. Thus, the non-linear optical values are enhanced for MR by reduction of dye solubility.

The absorbance of MR in DMSO-Water solutions at different percent of water in DMSO (between 0 and 90%) at a constant dye concentration $C_{\text{dye}} = 0.015$ mM are shown in the Fig. 5. A peak at 432 nm is observed at MR in DMSO solutions that this peak is Azo structure of MR. With increase of water in DMSO, a peak at 515 nm is observed, Fig. 5. The new peak in the DMSO-Water solutions comes from hydrazone in MR. So, an Azo to hydrazone change is observed with the increase of water.

Table 2 The nonlinear absorption (β), the nonlinear refractive index (n_2), second-order hyperpolarizabilities (γ_R), and the real part of the third-order susceptibility (χ_R) of the MR in different solvents (ethanol, DMSO, DMF)

Solvent	C dye (mM)	β ($\times 10^{-7}$ mw $^{-1}$)	n_2 ($\times 10^{-12}$ m 2 W $^{-1}$)	XR(3) ($\times 10^{12}$ m 3 W $^{-1}$ s $^{-1}$)	γ_R ($\times 10^{-10}$ m 6 W $^{-1}$ s $^{-1}$)
Ethanol	0.03	6.5 \pm 0.3	–	–	–
	0.026	5.8 \pm 0.2	–	–	–
	0.02	4.2 \pm 0.2	–	–	–
	0.015	2.4 \pm 0.1	–	–	–
	0.01	0.5 \pm 0.1	–	–	–
	0.008	–	11.1 \pm 0.5	7.2 \pm 0.3	5.5 \pm 0.2
	0.006	–	9.1 \pm 0.4	5.9 \pm 0.2	6.1 \pm 0.2
	0.004	–	7.0 \pm 0.3	4.5 \pm 0.2	7.0 \pm 0.3
	0.002	–	3.6 \pm 0.1	2.4 \pm 0.1	7.3 \pm 0.3
	DMF	0.025	6.8 \pm 0.3	–	–
0.02		5.8 \pm 0.2	–	–	–
0.015		4.8 \pm 0.2	–	–	–
0.012		2.7 \pm 0.1	–	–	–
0.01		0.5 \pm 0.01	–	–	–
0.008		–	14.5 \pm 0.6	23.6 \pm 0.9	14.8 \pm 0.6
0.006		–	12.2 \pm 0.5	19.9 \pm 0.8	16.7 \pm 0.7
0.004		–	8.7 \pm 0.3	14.1 \pm 0.7	17.8 \pm 0.8
0.002		–	2.9 \pm 0.2	4.7 \pm 0.2	19.1 \pm 0.9
DMSO		0.26	6.5 \pm 0.3	–	–
	0.02	6.0 \pm 0.3	–	–	–
	0.018	5.3 \pm 0.2	–	–	–
	0.015	3.5 \pm 0.2	–	–	–
	0.01	1.3 \pm 0.1	–	–	–
	0.006	–	13.7 \pm 0.6	40.9 \pm 1	29.8 \pm 0.9
	0.004	–	11.2 \pm 0.5	33.5 \pm 1	36.6 \pm 1
	0.002	–	5.9 \pm 0.3	17.7 \pm 0.8	38.9 \pm 1
	0.001	–	4.3 \pm 0.2	12.8 \pm 0.4	56.2 \pm 1

It is known that the wavelength of cw laser is far from the peak of absorption, the origin of change in the nonlinear refractive index, come from the thermal effect and it changes by the thermal conductivity. The thermo-optic coefficient can be gotten from the n_2 by the Eq. (5) (Azarpour et al. 2018):

$$n_{2thermal} = \left(\frac{dn}{dt} \right) \alpha \omega_0^2 / 4k \quad (12)$$

where α , k and dn/dt are the absorption coefficient, the thermal conductivity and the thermo-optic coefficient, respectively. In general, the α/k values, reduce with increasing of the solvent polarity, so the n_2 values decrease with the increase of solvent polarity.

The NLO properties of MR in Ethanol–Water solutions with surfactants are considered. The normalized open aperture curves of MR in Ethanol–Water (10% of Ethanol in Water) solution with change of AOT and CTAB concentrations are presented in Fig. 6. The value

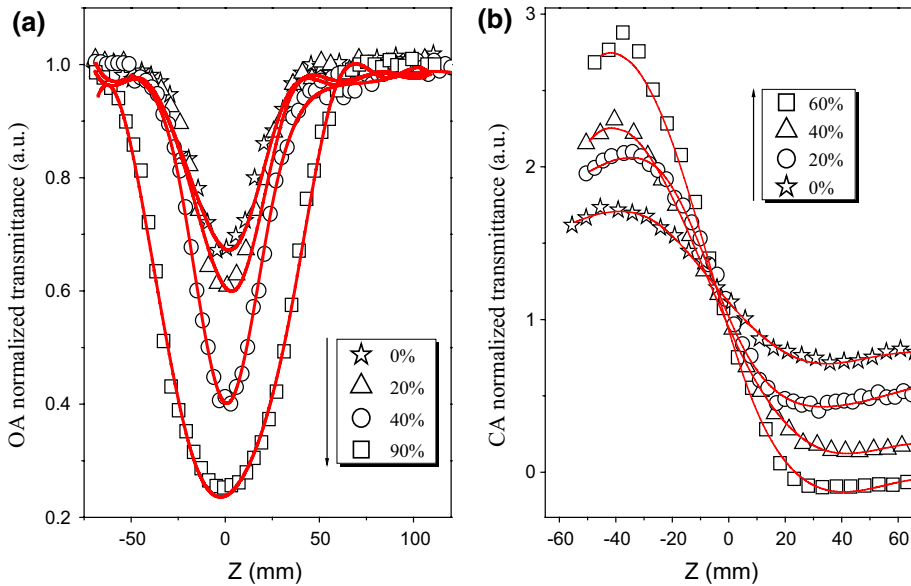


Fig. 4 **a** The open aperture and **b** close aperture curves of Methyl Red in DMSO-Water solutions at different percent of water in DMSO (between 0 and 90%) at a constant dye concentration ($C_{\text{dye}}=0.015$ mM for open aperture and $C_{\text{dye}}=0.006$ mM for close aperture)

Table 3 The nonlinear absorption (β), the nonlinear refractive index (n_2), second-order hyperpolarizabilities (γ_R), and the real part of the third-order susceptibility ($\chi_R^{(3)}$) of the Methyl Red in Water–DMSO solution at different water percent (0–90%)

C_{day} (mM)	Water (%)	ϵ	β ($\times 10^{-7}$ mw $^{-1}$)	n_2 ($\times 10^{-12}$ m 2 W $^{-1}$)	$\chi_R^{(3)}$ ($\times 10^{12}$ m 3 W $^{-1}$ s $^{-1}$)	γ ($\times 10^{-9}$ m 6 W $^{-1}$ s $^{-1}$)
0.015	0	47.6	2.6 ± 0.1			
	20	50.88	3.3 ± 0.1			
	40	54.16	5.0 ± 0.1			
	90	60.72	6.4 ± 0.1			
0.006	0	47.6		5.8 ± 0.2	17.2 ± 0.8	1.2 ± 0.6
	20	50.88		9.5 ± 0.4	32.1 ± 1.6	2.4 ± 0.1
	40	54.16		12.8 ± 0.6	48.7 ± 2.4	3.6 ± 0.1
	60	57.44		16.5 ± 0.7	70.6 ± 3.5	5.2 ± 0.2

of β is extracted and the results are presented in Table 4. In the MR mixed with Ethanol–Water–AOT solutions, the value of β is enhanced from 1.39×10^{-7} to 7.05×10^{-7} mw $^{-1}$ by the change of AOT from 0 to 4 mM. While, in the MR in Ethanol–Water–CTAB solutions, the value of β is reduced from 8.51×10^{-7} to 0.43×10^{-7} mw $^{-1}$ by the change of CTAB from 0 to 6 mM. With the increase of AOT concentration in solutions, the absorbance value change because of a hydrazone form of MR and it can increase the value of β . While, by the increase of CTAB concentration, the azo form of MR appears and it can reduce the β value.

Fig. 5 The absorbance of Methyl Red in DMSO-water solutions at different percent of water in DMSO (between 0 and 90%) at a constant dye concentration $C_{\text{dye}}=0.015 \text{ mM}$

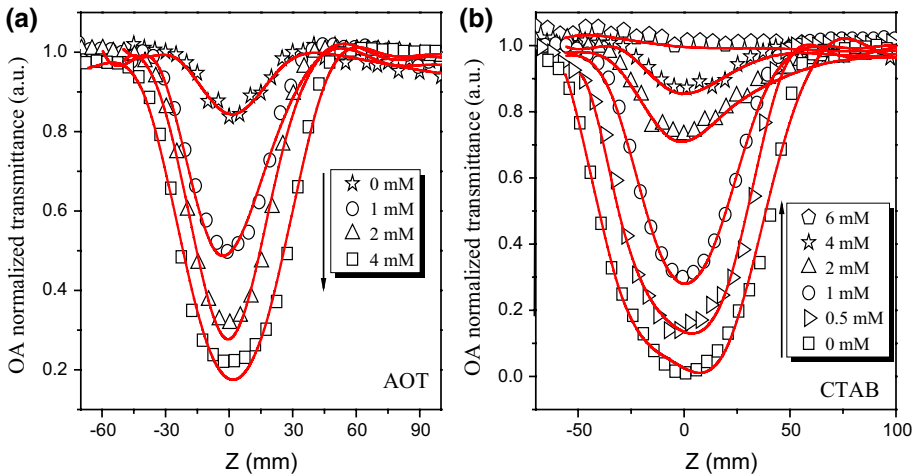
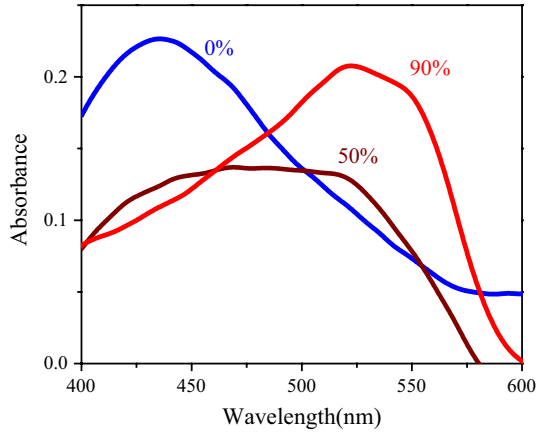


Fig. 6 The open aperture curves of Methyl Red in Ethanol–Water (10% of ethanol in water) solution at different **a** AOT and **b** CTAB concentrations and constant dye concentration ($C_{\text{dye}}=0.024 \text{ mM}$ for AOT solutions and $C_{\text{dye}}=0.043 \text{ mM}$ for CTAB solutions)

Table 4 The nonlinear absorption (β), of the Methyl Red in in Ethanol–Water (10% of ethanol in water) solution at different AOT and CTAB concentrations and constant dye concentration

Surfactant	C_{dye} (m M)	C_{Sur} (m M)	β ($\times 10^{-7} \text{ mw}^{-1}$)
AOT	0.024	0	1.3 ± 0.06
		1	4.4 ± 0.2
		2	6.2 ± 0.3
		4	7.0 ± 0.3
CTAB	0.043	0	8.5 ± 0.4
		0.5	7.3 ± 0.3
		1	6.06 ± 0.2
		2	2.2 ± 0.1
		4	1.2 ± 0.06
		6	0.4 ± 0.02

The effect of surfactant concentration on pH of Ethanol–Water solutions is studied. The study shows that the pH change from 6.38 to 5.95 with upsurge of AOT concentration from 1 to 4 mM and it change from 6 to 5.63 with an rise of CTAB concentration from 1 to 4 mM in Ethanol–Water solutions. From the results, the pH isn't changing too much with increase of surfactant concentration in solutions. In this part of work, the Ethanol–Water solutions is the solvent of the samples and the thermal conductivity of the doesn't change. So, the Azo to hydrazone is most reason to change of the nonlinear optical properties of MR.

In the previous work, a large enhancement of NLO parameters values is observed for component of merits by the change of the tetrathiafulvalene with two backside C=O groups. Generally, the increasing optical losses with enhanced linear absorption can change the NLO parameters (Fuks-Janczarek et al. 2005). The third nonlinear optical properties of benzodifuran-based derivatives have been studied by Z-scan techniques. The total third order NLO susceptibilities are due to the internal mechanisms (Kulyk et al. 2016).

The NLO response in iminopyridine complexes with Zn and Ag metal were studied via Z-scan techniques. The third order NLO susceptibilities of Zn containing complex were found to be higher than Ag containing one that it is due to the electronic distribution of component (Kulyk et al. 2016). In our case, the change of absorption spectra was observed in the tatorism, that it can change the NLO properties of MR and the change in absorbance could be due to change of electroc distribution of Azo to hydrozone form of MR molecular structure.

Previously, the Third Harmonic Generation investigation of metallophthalocyanine thin films was studied and it was demonstrated the annealing process can changes the NLO properties of metallophthalocyanine thin films that it is due to the low transition energy of excited state (Zawadzka et al. 2013). In the previous work, the NLO properties of two dimethylaminostyryl substituted BODIPY have been synthesized were studied. It was established that the absorption and fluorescence emission spectra are dependent on the conjugation length (Kulyk et al. 2016). In our case, the fluorescence intensity change, Fig. 2, that it can be due to change in the excited state of MR and it could be affect the NLO properties.

3.3 Absorbance and nonlinear optical properties of MR with α -amino acid

The distinguishing of amino acid concentration in the solution is one of the interesting topics. For this reason, the effect of α -amino acid concentration on the NLO properties of MR and Neutral Red is studied by Z-scan technique. The open aperture curves of MR in Ethanol–Water solution (10% Ethanol in Water) at different L-Phenylalanine and L-Alanine concentration at a constant dye concentration ($C_{\text{dye}}=0.024$ mM) are presented in Fig. 7a, b and the close aperture curves are shown in Fig. 7c, d. The values of β , n_2 , γ_R and χ_R are extracted from Fig. 7a and the results are summarized in Table 5. The results show, the nonlinear absorption values of MR reducing with the increase of α -amino acid concentration.

The previous study of the NLO properties of Rhodamine 6G and Erytrosin Y under different L-Alanine concentration is studied by z-scan instrument. The previous results shows that the nonlinear absorption of Rhodamine 6G and Erytrosin Y doesn't change with increase of L-Alanine concentration less than 1.6 mM (Pourtabrizi et al. 2018). In the present case, the L-Alanine concentration change from 0 to 5 mM and the more

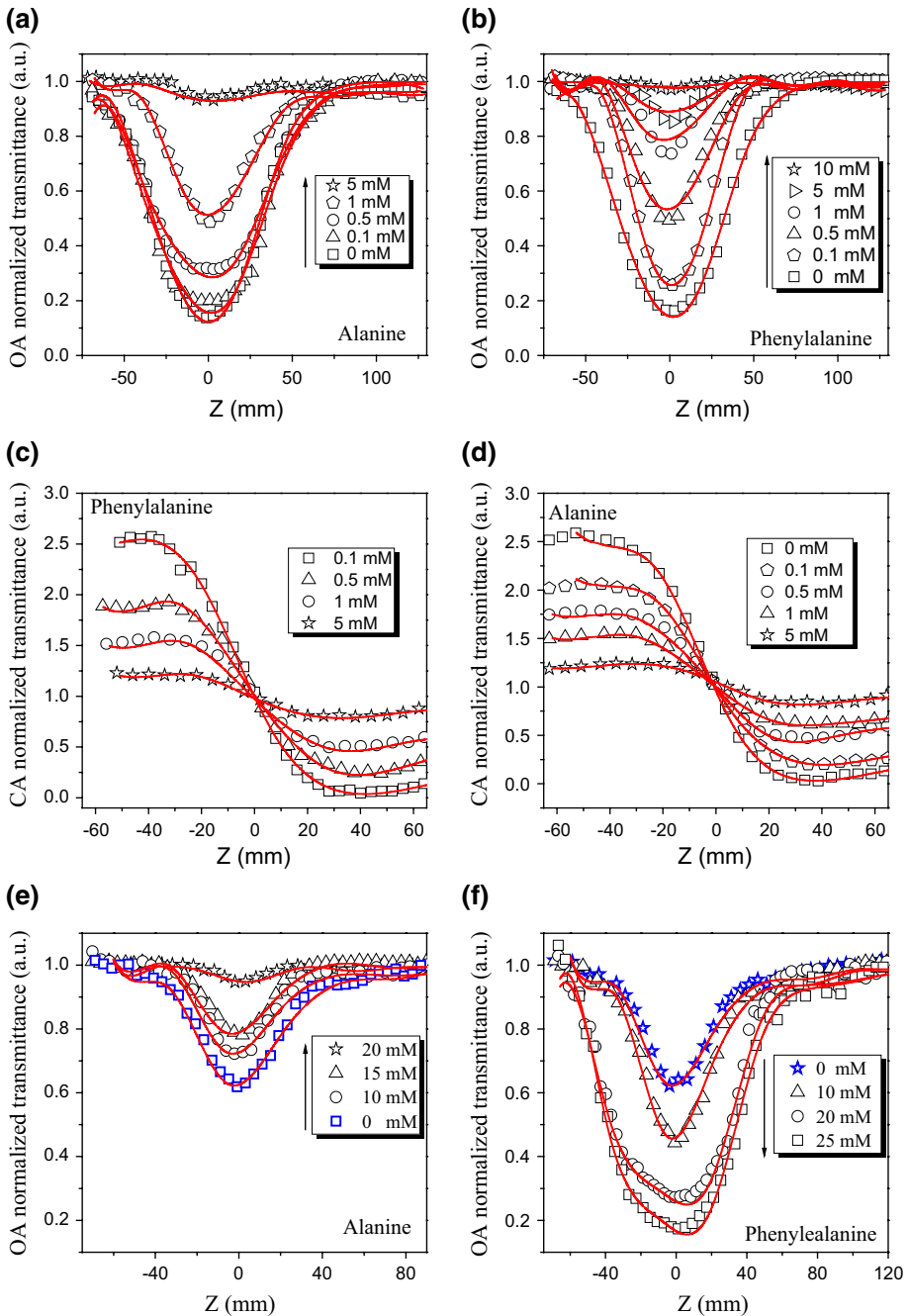


Fig. 7 The open aperture curves of MR in Ethanol–Water solution (10% ethanol in water) at different **a** L-Phenylalanine and **b** L-Alanine concentration at a constant dye concentration ($c_{\text{dye}}=0.024$ mM). The close aperture curves of MR in Ethanol–Water solution (10% ethanol in water) at different **c** L-Phenylalanine and **d** L-Alanine concentration at a constant dye concentration at a constant dye concentration ($c_{\text{dye}}=0.008$ mM). The open aperture curves of Neutral Red in Ethanol–Water solution (10% ethanol in water) at different **e** L-Phenylalanine and **f** L-Alanine concentration at a constant dye concentration ($C_{\text{dye}}=0.1$ mM)

Table 5 The nonlinear absorption (β), the nonlinear refractive index (n_2), second-order hyperpolarizabilities (γ_R), and the real part of the third-order susceptibility (χ_R) of the MR in Ethanol–Water solution (10% ethanol in water) at different L-Phenylalanine and L-Alanine concentration at a constant dye concentration

Amino acid	C_{dye} (mM)	$C_{\text{acid amine}}$ (mM)	β ($\times 10^{-7} \text{ mw}^{-1}$)	n_2 ($\times 10^{-12} \text{ m}^2 \text{ W}^{-1}$)	$\chi_R^{(2)}$ ($\times 10^{12} \text{ m}^3 \text{ W}^{-1} \text{ s}^{-1}$)	γ_R ($\times 10^{-10} \text{ m}^6 \text{ W}^{-1} \text{ s}^{-1}$)
Alanine	0.024	0	7.3 ± 0.2	–	–	–
		0.1	7.0 ± 0.2	–	–	–
		0.5	5.9 ± 0.1	–	–	–
		1	4.2 ± 0.1	–	–	–
		5	0.6 ± 0.02	–	–	–
		0	–	14.4 ± 0.7	9.8 ± 0.3	27.1 ± 0.9
		0.1	–	11.7 ± 0.5	8.0 ± 0.2	22.2 ± 0.8
		0.5	–	8.5 ± 0.4	5.8 ± 0.2	16.0 ± 0.7
		1	–	6.1 ± 0.3	4.1 ± 0.1	11.5 ± 0.5
		5	–	2.9 ± 0.1	2.0 ± 0.1	5.5 ± 0.4
Phenylalanine	0.024	0	7.2 ± 0.2	–	–	–
		0.1	6.4 ± 0.2	–	–	–
		0.5	4.3 ± 0.1	–	–	–
		1	1.9 ± 0.1	–	–	–
		5	1.0 ± 0.01	–	–	–
		10	0.1 ± 0.02	–	–	–
		0.1	–	14.27 ± 0.7	9.7 ± 0.3	26.8 ± 0.9
		0.5	–	11.7 ± 0.5	8.0 ± 0.2	22.0 ± 0.8
		1	–	7.7 ± 0.4	5.2 ± 0.1	14.5 ± 0.5
		5	–	3.1 ± 0.2	2.1 ± 0.1	5.9 ± 0.4

change on nonlinear optical properties of MR is observed for higher L-Alanine concentration in solution, Table 5.

In this work, the NLO properties of Neutral Red are studied and the results are compared with MR. The open aperture curves of Neutral Red in Ethanol–Water solution (10% Ethanol in Water) at different L-Phenylalanine and L-Alanine concentration at a constant dye concentration ($C_{\text{dye}} = 0.1$ mM) is presented in Fig. 7e, f. The value of β is extracted and the results are presented in Table 6. The results shows, the β value of Neutral Red reducing with the increase of L-Alanine concentration, while it enhances with the increase of L-Phenylalanine concentration.

The absorbance of MR in Ethanol–Water solution with and without α -amino acid, are presented in Fig. 8a. The absorbance peak of MR in Ethanol–Water solution shows two peaks at 428 nm and 515 nm that the peak at 428 nm is reduced and the peak at 515 nm is enhanced by the increase of L-Phenylalanine. The absorbance peak at 428 nm is enhanced by the increase of L-Alanine compared to the L-Phenylalanine solutions and the azo to hydration form is appeared by the increase of L-Phenylalanine concentration.

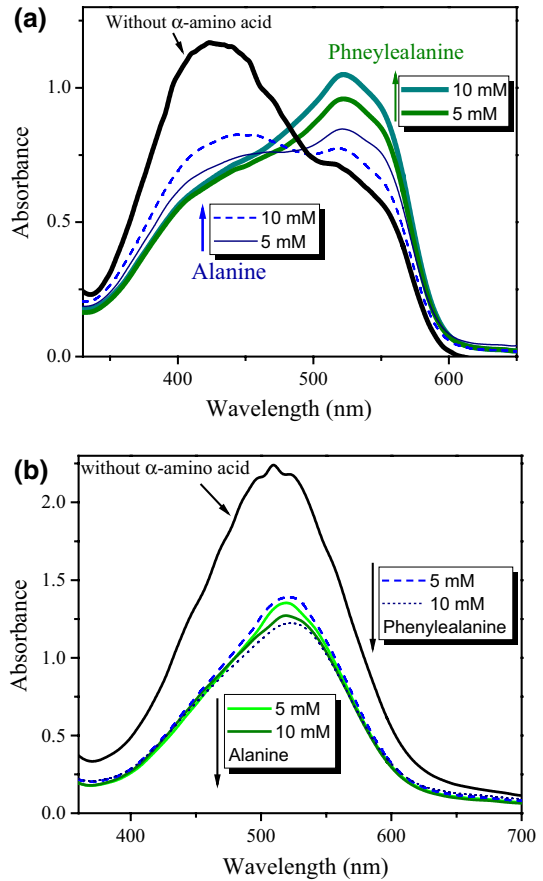
The absorbance of Neutral Red in Ethanol–Water solution with and without acid amine, are presented in Fig. 8b. The absorbance peak of Neutral Red in Ethanol–Water solution shows a peak at 510 nm that the value of absorbance is reduced by increase of amino acid concentration. It is recognized, L-Phenylalanine is hydrophobic and the solubility of L-Phenylalanine is less than L-Alanine in water and it doesn't change with adding salt to solutions (Hossain et al. 2017), and the aggregation of the L-Phenylalanine is more than the L-Alanine. By reason of its hydrophobicity, phenylalanine is closely found buried within a molecule and the π electrons of the phenyl ring. Thus, the interaction between phenylalanine with surfactant is higher than alanine. The differences between L-Phenylalanine and the L-Alanine can produce different behavior in the nonlinear optical properties of Neutral Red.

The effect of α -amino acid concentration on the pH of Ethanol–Water (10% of Ethanol in Water) is studied. The study shows that the pH variation from 6.8 to 6.3 with increase of L-Alanine concentration from 1 to 5 mM and the pH is constant at 6.07 with an increase of CTAB concentration from 1 to 5 mM. Thus, the variation of pH isn't too much and the electrostatic interaction between MR with L-Alanine to L-Phenylalanine is the most reason for transfer of Azo to hydrazone structure.

Table 6 The nonlinear absorption (β) of Neutral Red in Ethanol–Water solution (10% ethanol in water) at different L-Phenylalanine and L-Alanine concentration at a constant dye concentration

Amino acid	C_{dye} (mM)	$C_{\text{acid amine}}$ (mM)	β ($\times 10^{-7}$ mw $^{-1}$)
Alanine	0.1	0	3.3 \pm 0.1
		10	2.4 \pm 0.1
		15	1.9 \pm 0.04
		20	0.4 \pm 0.02
Phenylealanine	0.1	0	3.3 \pm 0.1
		10	4.8 \pm 0.2
		20	6.0 \pm 0.2
		25	6.9 \pm 0.3

Fig. 8 **a** The absorbance of MR in Ethanol–Water solution with and without α -amino acid. **b** The absorbance of Neutral Red in Ethanol–Water solution with and without acid amine



4 Conclusions

This study demonstrates the effect of various organic solvents (ethanol, DMSO and DMF), amino acids (*L*-Phenylalanine and *L*-Alanine) and ionic surfactants (CTAB and AOT) on linear and nonlinear optical (NLO) properties of Methyl Red (MR) by the *z*-scan, absorbance and fluorescence spectroscopy. The azo-hydrazone tautomerism form of MR is observed by the change of CTAB to AOT or adding the *L*-Phenylalanine and *L*-Alanine. While azo-hydrazone switching is not observed with solvent polarity. With the provision of the quantum perturbation theory, it is demonstrated that the dipole moment ratio of hydrazone form is higher than azo form. The NLO properties of MR can be changed by the solvent, surfactant charge effect and α -amino acid in solutions. The results can be integrated to show the significance of MR as a good candidate for the detection of *L*-Phenylalanine and the *L*-Alanine in the solution.

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